SCIENCE FOR GLASS PRODUCTION

EFFECTIVENESS OF SULFATE CLARIFICATION OF TYPE E ALKALI-FREE GLASS

N. F. Zhernovaya,[1] N. I. Min'ko,[1] V. I. Onishchuk,[1] M. Yu. Kochetov,[1] and S. A. Borodkin[1]

Clarification of type E alkali-free glass (production of glass beads and continuous glass fiber) with sodium sulfate was investigated in comparison to antimonous anhydride and cerium dioxide. The high effectiveness of sulfate clarification was demonstrated and the process parameters for using it were determined.

Glass fibers and materials made from them are widely used for reinforcing polymer and ceramic matrices due to the simplicity of manufacture, low cost, and acceptable physicochemical properties. The fibers are made from glass of different compositions, and type E glass is most in demand throughout the world; it contains (%[2]): 53 – 57 SiO_2, 5 – 8 B_2O_3, 13 – 15 Al_2O_3, 0.5 – 2.5 MgO, 20 – 26 CaO, 0.2 – 0.8 R_2O, 0.45 – 0.6 Fe_2O_3, 0 – 0.6 F [1] and has high dielectric indexes, mechanical strength, and chemical stability.

E glass initially contained no boron oxide. Considering its wide use for production of reinforcing elements for plastics and concretes (complex filaments, rovings, mesh, fabrics), the composition was developed as cheap and accessible. The batch was based on natural materials: sand, clay (kaolin), chalk (lime), dolomite. Later B_2O_3, which is a good flux and at the same time improves the strength and dielectric properties of the glass, was added to the composition to decrease the founding and formation temperature [2]. It is most rational to add 5 – 8% B_2O_3. In this case, its positive effect on the process and performance properties of the glass is maximum, while the volatility is relatively low during founding (in gas-flame furnaces, it does not exceed 8%, versus 15% at high concentrations of boron oxide).

The coefficients of the Vogel – Flucher – Tamman (VFT) equation for the temperature dependence were determined with the known values of the temperature characteristics (formation, Littleton, and glass transition) of boron-containing E glass [3]:

$$\log \eta = -6.98 + \frac{8788.4}{(T - 201.1)}.$$

The calculation with this equation is in good agreement with the published data from experimental measurements of the viscosity of E-glass at high temperatures (Fig. 1). Due to the presence of calcium and boron oxides in E-glass, the melt viscosity becomes lower than the melt viscosity of sheet glass beginning with the temperature of 1200°C and higher. Nevertheless, accelerants and clarifiers are used to accelerate founding of E-glasses.
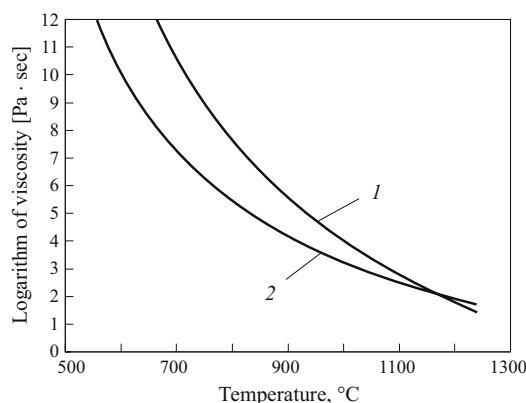

Fig. 1. Temperature dependence of the viscosity of E-glass: *1*) with the VFT equation; *2*) float glass.

[1] V. G. Shukhov State Technical University, Belgorod, Russia; Tver'stekloplastik Co., Tver', Russia.

[2] Here and below, mass content.

Expensive, scarce, and toxic materials are frequently used to clarify E glass. For example, at Tver'stekloplastik Co., beads made from E glass are used to manufacture fiberglass and materials based on it. Antimony(III) oxide complexed with saltpeter was initially used as E-glass clarifiers at the company, then attempts were made to use cerium dioxide. It should be noted that in addition to the toxicity, the antimony(III) oxide acquired by Tver'stekloplastik Co. at Ryazan'tsvetmet Co. is expensive. The cost of 1 ton of this clarifier was 120,000 – 150,000 rubles, which negatively affected the cost of the glass beads as a result.

In our opinion, this kind of additive should not be used in mass-production glass technology and an alternative should be sought. Of the available and inexpensive clarifiers, sodium sulfate is of interest, as its positive role in the final stage of founding glasses of different compositions has been confirmed by many laboratory and industrial experiments [4, 5].

The mechanism of sulfate clarification of glass can be represented as follows [6]. When the batch is heated, the organic impurities in the batch (the relative amount can be characterized by the value of the chemical oxygen demand of the batch, expressed in mg O_2 per 100 g of material) partially liberate carbon, which reacts with the carbon dioxide formed in decomposition of carbonates or with atmospheric oxygen at a temperature of 600 – 900°C:

$$C + CO_2 \rightarrow 2CO;$$

$$2C + O_2 \rightarrow 2CO.$$
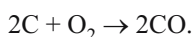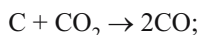
The reactions of the batch components with carbon(II) oxide shift the equilibrium between the oxidized and reduced forms of polyvalent elements toward the more reduced state:

$$2Fe^{3+} + O^{2-} + CO \rightleftarrows 2Fe^{2+} + CO_2;$$

$$SO_4^{2-} + CO \rightleftarrows SO_2 + CO_2 + O^{2-}. \qquad (1)$$

Some of the unreacted sulfate decomposes at temperatures above 1400°C and has an effective clarifying effect:

$$SO_4^{2-} \rightleftarrows SO_2 + O^{2-} + \frac{1}{2}O_2. \qquad (2)$$
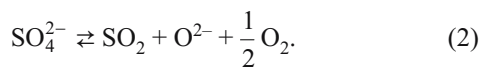
Precise balance of the sulfate in the glass is very important for quality sulfate clarification. The optimum amount of sulfate added is calculated as the sum of the constituents:

sulfate losses in the initial stage of founding — reaction (1);

solubility of SO_3 in the glass at the maximum founding temperature;

amount of sulfate required for clarification — reaction (2).

In sodium-calcium silicate glasses, these processes have been relatively well investigated. For example, we know that for an initial amount of SO_3 in the glass equal to 0.66% (we use 100% for the relative initial content), there is 0.55 – 0.53% SO_3 in the glass melt at the beginning of the clarifica-

TABLE 1

Batch	Clarifier	Mass content, %	RDP* of batch
F/Sb	Sb_2O_3 ($NaNO_3$)	0.17	+ 31.0
F/Ce	CeO_2 ($NaNO_3$)	0.12	+ 36.0
M/S-0.13	SO_3	0.13	+ 7.9
M/S-0.26	SO_3	0.26	+ 16.6
M/S-0.39	SO_3	0.39	+ 25.4
M/0	–	–	– 1.0

* The redox potential of the batch was obtained by calculation [7].

tion process, so that SO_3 losses in the initial stage of founding are 0.11 – 0.13% (16 – 19% of the initial content). Then 0.32 – 0.15% SO_3 (48 – 23% of the initial amount) is dissolved in the clarified glass melt, which means that 0.23 – 0.38% is lost for clarification, i.e., 35 – 58% of the initial SO_3 content [6].

E-glass has been investigated very little in this direction, but we know that the solubility of sulfate in it is much lower than in sodium-calcium-silicate glasses and after clarification, approximately 0.01% SO_3 remains in E-glass. If we set the sulfate losses in the initial stage of founding and clarification costs equal to those for sodium-calcium-silicate melts, the amount of SO_3 in the E-glass batch will not exceed 0.35 – 0.40%. The problem thus consists of determining the amount of sulfate that has an effective clarifying effect and does not complicate the course of founding of the E-glass.

The studies were based on the statistical average composition of Tver'stekloplastik Co. glass, established by statistical processing of the results of running chemical analyses for 2006.

Statistical Average Composition of E-Glass

Mass content, %	Standard deviation
52.45 SiO_2	0.28
0.27 TiO_2	0.04
8.65 B_2O_3	0.21
14.93 Al_2O_3	0.18
0.41 Fe_2O_3	0.03
0.57 MgO	0.08
21.18 CaO	0.18
0.37 Na_2O	0.03
0.19 K_2O	0.04
0.30 F	0.02

Tver'stekloplastik Co. production batches (standards) and model batches prepared from factory raw material were used; BS-050-1 quartz sand (GOST 22551–77), ground dolomite (TU 5743-005-21079129–00), KE-2 dry concentration kaolin (TU 5729-070-00284530–96), type A, grade 1 conversion chalk (TU 113-08-667–98), type B boric acid (GOST 18704–78), type FF-95-B fluorspar (GOST 22219–91). Six glass batches were investigated: two factory and four model (see Table 1).
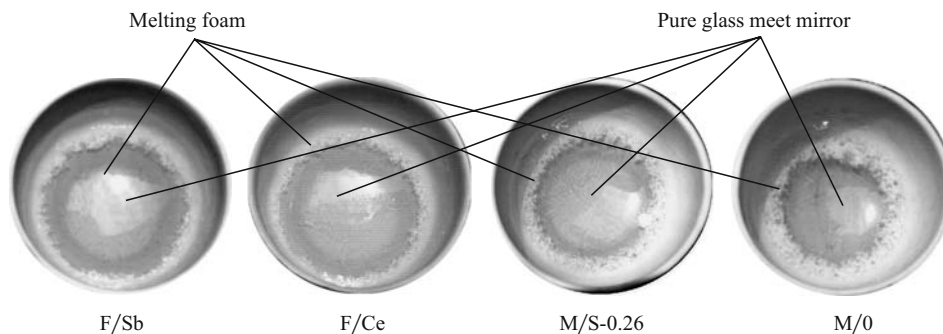
Fig. 2. External appearance of crucibles with batches after heat treatment at 1300°C.

Briquets (20 mm in diameter, 30 mm high, weighing approximately 20 g), which were placed in 50-ml corundum crucibles and underwent polythermal treatment in the 900 – 1300°C range with a step of 100°C and were held at each temperature for 1 h, were prepared from the batches by tamping. Heat treatment at 900 and 1000°C did not cause any marked changes in the external appearance of the briquets. At 1100°C, a melt whose surface was totally coated with silica foam appeared in all of the crucibles, and the surface state of the glass melt differed significantly at 1300°C (Fig. 2) due to the effect of small additives.

At 1300°C, the effect of the Sb_2O_3 and CeO_2 clarifiers were most effective. We know that decomposition of antimony(V) oxide and cerium dioxide begins at 1000 – 1100°C and is accompanied by liberation of oxygen, which causes mixing and clarification of the glass melt. As a result of this, less foam remained on the surface in the crucibles with the F/Sb and F/Ce batches than in the crucible with the M/S-0.26 batch, where the batch containing sodium sulfate as clarifier was treated with heat. At the same time, we know that the effective clarifying effect of sulfate begins at minimum temperatures of 1400°C and consequently is fully manifested in an industrial furnace in which the maximum glass melt temperature is 1500°C (1560°C crown temperature).

In laboratory founding, 240-ml corundum crucibles (50 mm in diameter and 120 mm high) with a small amount of batch (approximately 50 g) were placed in an electric resistance furnace with silicon-carbide heaters and heated to 1400°C. The crucibles were recharged with batch briquets sintered at 1000°C twice in the 1400 – 1450°C range. Then the temperature was raised to 1500°C over 30 min and held there for 40 min. The furnace was then cooled to 1250°C and the crucibles were removed and transferred to a muffle for annealing.

All of the batches founded satisfactorily, and the surface of the glass was clean with no foam (except for the batch with no clarifier). At the same time, in examining the inner walls of the crucibles, significant foaming of compositions M/S-0.39 and M/S-0.26 was detected (the foam rose to the upper edge of the crucible), probably due to an excess of sulfate. The foam rise height in M/S-0.13 glass was at the level of the factory compositions.

Two cubic samples ($10 \times 10 \times 10$ mm) with a polished surface were prepared from the massive chunks of glass of each composition obtained. Visual and microscopic analysis of the amount, size, and character of distribution of glass bubbles in the glasses led to the following conclusions. Gas bubbles smaller than 0.8 mm remaining in the glasses were of the order of seeds. Glass of composition M/S-0.13 had the minimum amount of gas inclusions. The quality of clarification of compositions M/S-0.26 and M/S-0.39 corresponding to factory compositions F/Sb and F/Ce.

Effective clarification of glass melts with moderate foaming during founding is thus ensured by the presence of a maximum of 0.2% SO_3 in E-glass. It is necessary to recall that this amount of sulfate consists of the SO_3 specially added to the glass with sodium sulfate (0.13%) and the SO_3 contained in the basic raw materials, primarily the kaolin (0.066%). In view of the small amount of effective sulfate and the necessity of precisely measuring it, the SO_3 content in the raw materials must be monitored and the amount of sodium sulfate in the batch must be corrected as a function of this.

The studies form the basis for examining the question of using an effective sulfate clarifier in production of E-glass at Tver'stekloplastik Co. This allows eliminating not only the expensive materials (Sb_2O_3 and CeO_2) but also the sodium nitrate, which provides for their clarifying power, from the batch. In sulfate clarification, sodium nitrate is not useful with respect to both the mechanism of the process and maintaining a rational redox potential of the glass.

The optimum concentration of sodium sulfate could be corrected slightly during the industrial tests to be conducted at Tver'stekloplastik Co. in the near future. Adding carbon to the batch composition is not recommended in view of the small amounts of sodium sulfate and the high chemical oxygen demand of the natural raw materials (in the case examined, from 120 for sand to 135 mg O_2/100 g for kaolin).

On the whole, technically competent industrial incorporation of sulfate clarifier in E-glass at Tver'stekloplastik Co. will allow increasing the technical and economic indexes of production of glass beads and fibers.

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